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THE CATALYTIC EFFECT OF CERTAIN METALS ON THE DEGRADATION
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NORMAN S. THOMPSON AND HUGH M. CORBETT

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The Institute of Paper Chemistry, Appleton, Wisconsin, U.S.A.

Methyl α -D-glucopyranoside (M α G) was oxidized in a Teflon lined reactor with approximately 3 mM oxygen in 1.25N NaOH in the presence and absence of metal strips of copper, cobalt, steel, tungsten, platinum, silver, nickel, zirconium or titanium. All metals but Pt, Ni, Zr, and Ti increased the production of peroxides in a manner indicating glycoside degradation had occurred. Analysis of the Co and steel catalyzed reactions confirmed the greater loss of M α G compared to the control in those instances. The presence of Ni, Zr, and Ti had the least effect of any metals tested on the degradation of M α G and production of peroxides. Platinum exhibited a stabilizing effect upon M α G degradation and the mechanistic differences between this stabilization and those proposed for the stabilizing action of magnesium ions is discussed. Methyl β -D-glucopyranoside exhibited similar behavior to M α G with nickel considered to be the least catalytic metal by these criteria.

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INTRODUCTION

Research was conducted to discover noncatalytic metals for use in an experimental high pressure reactor designed to investigate the autoxidation of model substances representing wood components¹. We speculated that the high surface-to-volume ratio of the experimental reactor (which employs capillary tubing) would favor catalytic reactions compared to the smaller ratio of commercial installations of similar composition. For this reason, catalytic autoxidation of carbohydrates would be greater in small scale reactors. The difference in behavior between the two could only be minimized by choosing less catalytic construction materials for the experimental device.

The evaluations were made by reacting methyl α -D-glucopyranoside (M α G) and (in some instances) methyl β -D-glucopyranoside (M β G) in 1.25N NaOH in a Teflon-lined reactor² with approximately 3 mM oxygen in the presence and absence of test strips of metal. The loss of methyl glucoside and the formation of organic and hydrogen peroxide were the only parameters measured, since previous research demonstrated the dependence of other reaction products and pathways on the presence and quantity of these components³⁻⁷. Agreement between the rates of loss of methyl glucosides and formation of peroxides in the test reactions and controls would be considered evidence for the absence of catalysis.

¹ N.S. Thompson, J.W. Green, and H.C. Corbett. Research to be presented at the CPPA-CIC Wood Chemistry Conference in Vancouver, B.C. Sept. 1979.

² J.T. McCloskey, J.D. Sinkey, and N.S. Thompson. 1974 Nonsulfur Pulping Symposium, p. 5-10; Tech. Assoc. Pulp Paper Ind. (Madison), Oct. 16-18, 1974.

³ J.T. McCloskey, J.D. Sinkey, and N.S. Thompson, Tappi 68, 56 (1975).

⁴ J.D. Sinkey and N.S. Thompson, Paperi Puu 56, A73 (1974).

⁵ J.T. McCloskey, L.R. Schroeder, J.D. Sinkey, and N.S. Thompson, Paperi Puu 57, 131 (1975).

⁶ J.W. Weaver, L.R. Schroeder, and N.S. Thompson, Carbohyd. Res. 48, C5 (1976).

⁷ R.H. Millard, L.R. Schroeder, and N.S. Thompson, Carbohyd. Res. 56, 259 (1977).

RESULTS

Published information by many investigators indicate most transition metal ions enhance degradation of cellulose and cellulose models during autoxidation in alkali. (For excellent reviews see References 8 and 9.) The extent of degradation is related to the type of metal ion, its concentration, and its valence. Previous experiments in this laboratory indicated Cu^{+2} , Fe^{+3} , and Co^{+2} catalyze the decomposition of $\text{M}\alpha\text{G}$ and $\text{M}\beta\text{G}$ with the formation of large quantities of organic peroxides^{2-5,10}. Nickel (+2) ions had no detectable effect upon the rate of degradation of $\text{M}\alpha\text{G}$ nor on the formation of hydrogen peroxide and organic peroxides².

When Cu, Fe, Co and No. 316 stainless steel strips were tested, coloration of the spent liquors suggested the presence of metal ions. We assumed that metal ion catalysis had occurred as described previously^{2-6,8,10}. The Co and steel catalyzed reactions were worked up to confirm this speculation. The data plotted in Fig. 1 agree with previous results, indicating that little if any hydrogen peroxide is formed as a result of Co and stainless steel catalysis. Analysis of the spent liquors indicated the presence of 7 p.p.m. ferric ion in the latter case.

Oxidation in the presence of platinum metal did not result in the formation of as much hydrogen peroxide as found in the control reaction. Oxidation in the presence of tungsten metal caused very large quantities of hydrogen peroxide to be formed and tungstic acid was isolated from the reaction mixture.

⁸R. Malinen, Paperi Puu 57, 193 (1975).

⁹E. Sjostrom and O. Valttila, Paperi Puu 69, 37 (1978); 54, 695 (1972).

¹⁰J.W. Weaver, L.R. Schroeder, and N.S. Thompson, Paperi Puu, in press.

Oxidation in the presence of Ni, Zr, Ti, and Ag metal catalysts did not produce quantities of hydrogen peroxide differing greatly from that produced in their absence (control), nor were significant quantities of their ions found in the spent liquors.

The formation of organic peroxides during these reactions is shown in Fig. 2. These peroxides are a measure of the acid resistant peroxidic components and are measured by the increase in color after 18 hours reaction with acidified titanous ion. Large quantities are generated when Ag, W, No. 316 stainless steel, and Co strips are present. Although these peroxides are associated with the occurrence of excessive glycoside degradation, they are not considered to be the cause of carbohydrate degradation²⁻⁵. On the other hand, Ni, Zr, and Ti generate about the same quantities of organic peroxide as the control. Platinum does not catalyze the formation of as much peroxide as the control suggesting it catalyzes oxidation in a unique manner.

The plots in Fig. 3 demonstrate that the presence of Ni, Zr, and Ti metal strips do not appreciably alter the rate of degradation of MαG by oxygen and alkali. The rates of degradation of MαG in the Pt and Co metal catalyzed reactions are different than the control reaction. The enhanced degradation caused by Co is in agreement with results anticipated from the literature^{8,9}. The lessened degradation of MαG in the presence of Pt is unexpected since that metal catalyzes peroxide decomposition. With the exception of Pt catalysis, the peroxide levels of the catalyzed reactions observed in Figs. 1 and 2 are in agreement with the data shown in Fig. 3.

Significant differences in the rates of alkaline degradation of M α G and M β G are observed in the absence of oxygen¹¹ and only small differences have been observed between their rates of degradation in uncatalyzed autoxidation reactions¹². The reaction products are approximately the same when oxygen is present. This suggests that rate rather than mechanistic differences exist between the two glycosides during autoxidation. The slightly different quantities of peroxides formed from the M β G autoxidation compared to the M α G autoxidation reflects this small difference in reactivity observed by others¹². The results demonstrate that the catalytic action of Ni on M β G is similar to its effect on M α G. Zirconium on the other hand does catalyze the formation of greater quantities of both peroxides.

DISCUSSIONS AND CONCLUSIONS

In the absence of suitable capillary tubing, nickel, and to a lesser extent, Zr, and Ti metals satisfy present criteria for a noncatalytic reactor metal because their action on M α G and M β G does not differ greatly from the reaction in their absence. This behavior of Ni might be anticipated from the literature^{13,14}. No data is available describing the action of the other two metals. Most other metals studied - Ag, Co, and No. 316 stainless steel - decompose hydrogen peroxide and increase the amounts of other stable organic peroxides. Some of these metals are oxidized during the reaction and the harmful effect of the resulting ions (both soluble and insoluble) could account for the observed behavior.

¹¹E. Dryselius, B. Lindberg, and O. Theander, Acta Chem. Scand. 12, 340 (1958).

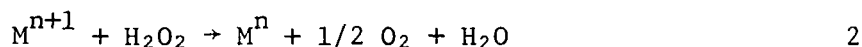
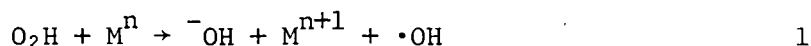
¹²R. Malinen and E. Sjostrom, Cellulose Chem. Technol. 9, 231 (1975).

¹³L.L. Landucci and N. Sanyer, Tappi 58, 60 (1975).

¹⁴A.F. Gilbert, E. Pavlovova, and W.H. Rapson, Tappi 56, 95 (1971).

The mechanisms by which the metals and/or their ions catalyze decomposition is not clearly understood. The metal ions must be capable of being oxidized or reduced. The stability of hydrogen peroxide in 1.25N NaOH at room temperature in the presence and absence of these metals was investigated in an attempt to understand these mechanisms. The data summarized in Table 1 show that changes in the degradations of MαG in the presence of these metals are clearly paralleled by changes in the stability of sodium peroxide itself in their presence.

In the case of the catalytic action of transition metals and their ions, this parallel can be rationalized if we assume that the decomposition of peroxide to hydroxyl and perhydroxyl radicals by the Haber and Weis reaction¹⁵ ultimately leads to glucoside degradation.



Radicals from peroxides and oxygen bring about degradation by oxidizing anhydrosugar units to hydroxyhydroperoxides^{2,6,7,10}. The metal ions can further accelerate the degradation by decomposing hydroxyhydroperoxides to hydroxyl and organic radicals capable of further reaction^{7,10,16}. This sets up a chain reaction which is quickly followed by terminating reactions^{2-5,7}. The reactions with metal ions can occur at solid-liquid interfaces as well as in solution.

Metallic Pt, on the other hand, diminishes the quantities of both hydrogen peroxide and dialkyl peroxides in solution besides minimizing the degradation of MαG. This parallels the behavior of magnesium ion on MβG under similar circumstances reported by Sinkey³⁻⁵

¹⁵ F. Haber and J. Weis, Proc. Roy. Soc. Ser. A, 147, 332 (1934).

¹⁶ D.O. Hearne. Ph.D. Thesis, The Institute of Paper Chemistry, 1978.

and differs because the concentration of hydrogen peroxide produced during the reaction does not increase above that of the control. The degradation of peroxide in the presence of magnesium ion is hindered because radical decomposition reactions are minimized^{8,9}. As a result the rate of degradation of glycosides is initially slow, but it increases as the peroxide level builds to an equilibrium value between the amount of peroxide formed and the amount decomposed. At that point, the rate of degradation of the glycoside (or cellulose) can become equal to that of the unstabilized reaction³⁻⁵.

The mechanisms by which the radical decompositions of peroxides are minimized are subject to great controversy. Magnesium stabilization may occur by the absorption of metal ion impurities onto magnesium hydroxide¹⁷. On the other hand, magnesium complexes with oxidized carbohydrate are postulated¹⁸ and the possibility of organic peroxide magnesium complexes limiting the effect of metal ions on organic peroxides cannot be excluded⁶.

These rationalizations are insufficient for the following reasons. The results of the interaction of oxygen and Mg in the presence of ferric or chromic ions and varying amounts of magnesium ions described elsewhere² show that hydrogen peroxide levels can be increased and organic peroxide levels diminished, in agreement with the sorption theories. The interaction of cobaltous and cupric ions under identical circumstances shows that hydrogen peroxide production is not initiated even with a 186-fold excess of magnesium ion.

¹⁷

J. D'Ans and J. Mattner, Angew. Chem. 64, 16, 448 (1952).

¹⁸

J. Defaye and A. Gadelle, Pulp Paper Can. 75, T394 (1974); J. Defaye, H. Driguez, and A. Gadelle, Carbohydr. Res. 38, C4 (1974).

The behavior of Pt metal presents yet another example of anomalous behavior. The low levels of both hydrogen peroxide and dialkyl peroxides suggest that the elimination of peroxide formation and/or decomposition of peroxides by nonradical pathways prevents the onset of chain oxidization. Peroxide decomposition might occur by two sequential electron transfers while the peroxide is sorbed onto the surface of the Pt. Thus, while slow oxidation can occur, catalytic action will be inhibited until the surface of the Pt is poisoned toward peroxide reduction.

EXPERIMENTAL

The apparatus used for this investigation was the Teflon-lined 1-liter reactor designed by McCloskey and Sinkey²⁻⁵. It was operated in the manner described elsewhere². Test metal strips purchased from Ventron Corp. cut to 1 x 6 inches were attached to the Teflon baffle within the reactor. Methyl α -D-glucopyranoside, and in a few instances methyl β -D-glucopyranoside, was reacted with 1.25N sodium hydroxide and 0.682 mPa oxygen at 120°C for different times in the reactor with and without the strips present. The reaction was quenched by cooling, and the contents were analyzed for unreacted glycoside by gas chromatography. Hydrogen peroxide and organic peroxides were analyzed by conventional techniques²⁻⁵ in which hydrogen peroxide was measured by the initial color formed in the presence of titanium sulfate and organic peroxides were measured by the increase in color after 18-hr testing. The dissolved metal contents of the liquors were measured by flame photometry.

The concentration of dissolved oxygen under these conditions in parallel experiments was found to be 3 mM¹⁶ and was achieved within 1 hour of application. The analysis was performed in a modified Winkler apparatus and will be reported at a later date.¹

The stability of alkaline peroxide solutions to certain of these metals at room temperature was tested by suspending the metal strips in

their Teflon holders in a stirred alkaline peroxide solution composed of 500 mL triply distilled water, 25 g NaOH, and 1 mL of 14% H_2O_2 . Samples were removed at intervals for peroxide analysis (see Table 1).

Before they were tested, all metals were soaked in water and organic solvents to remove soluble surface impurities. Several metals such as vanadium and molybdenum developed highly colored oxides on their surfaces during the water treatment and consequently were not evaluated further, since it was feared they would corrode severely in alkali.

The metals evaluated were stainless steel (No. 316), copper, iron, nickel, cobalt, titanium, tungsten, zirconium, platinum, and silver. Certain spent alkaline solutions were analyzed for dissolved metals. The control solution contained 5.9 p.p.m. iron, 2.1 p.p.m. aluminum, and 0.69 p.p.m. copper, introduced from impurities in the reagent-grade caustic. No increases in nickel, titanium, and zirconium were noted in the spent alkaline solutions when those metals were used on catalysis while all other liquors yielded 7 to 10 p.p.m. of the corresponding ion.

Table 1

Effect of Metal Strips on the Decomposition
of H₂O₂ in 1.25N NaOH

| | % Peroxide after 24 hr | Relative effect of metal ^a on decomposition of Mg by O ₂ |
|-------------------|---------------------------|---|
| Control | 87 | 0 |
| Stainless steel | 73 | - |
| Silver | 32 | - |
| Platinum | 30 | + |
| Nickel | 88 | 0 |
| Titanium | 87 | 0 |
| Zirconium | 87 | 0 |
| Tungsten | 100 | Not analyzed |
| Magnesium sulfate | 100 | + ^b |

a 0 no difference from control;

- less Mg than control;

+ more Mg than control.

b Tested on Mg³⁻⁵.

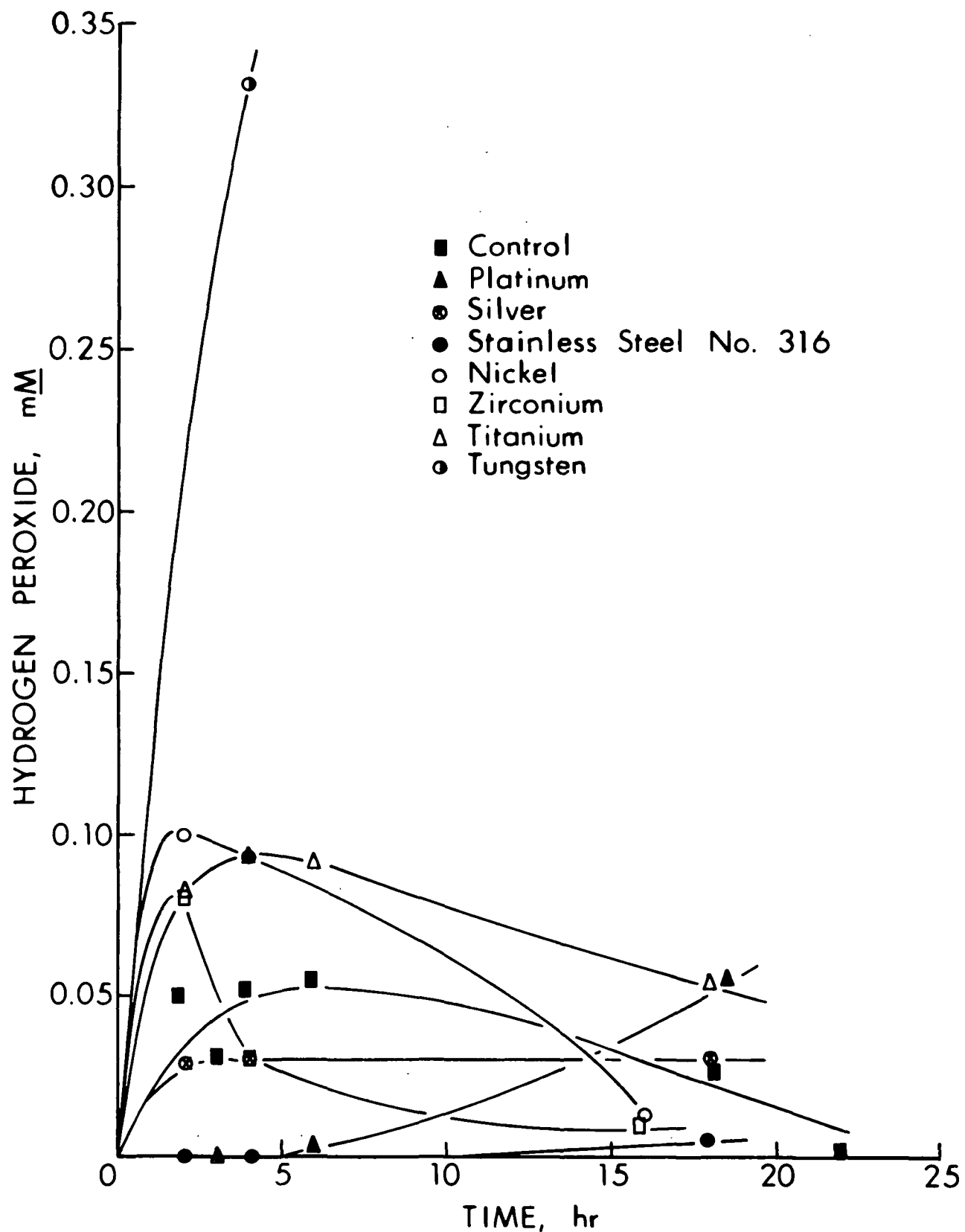


Fig. 1. The production of hydrogen peroxide from the reaction of methyl α -D-glucopyranoside with oxygen and alkali in the presence of different metals

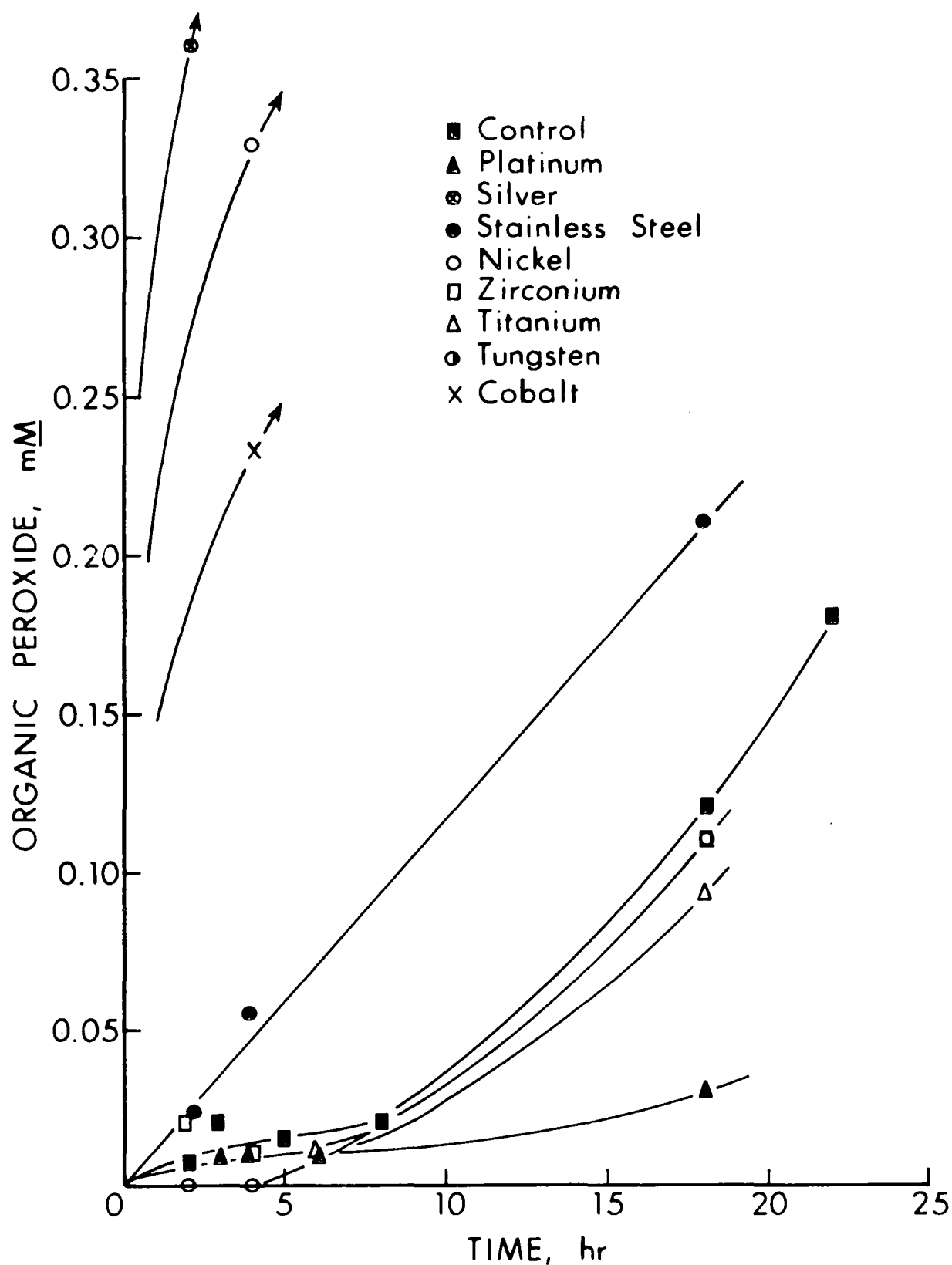


Fig. 2. Production of organic peroxides from the reaction of methyl α -D-glucopyranoside with oxygen and alkali in the presence of different metals

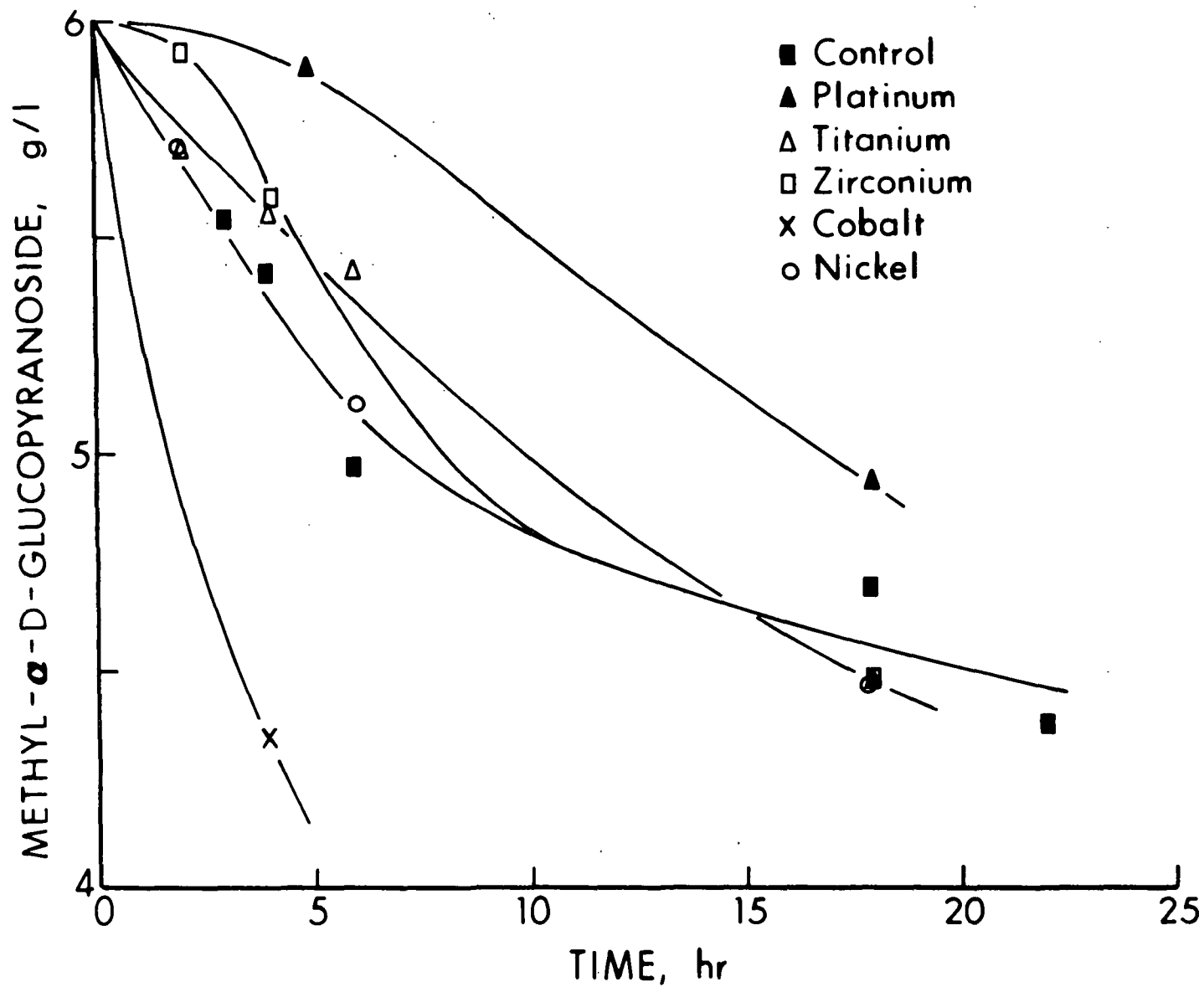


Fig. 3. The loss of methyl α -D-glucopyranoside during reaction with oxygen and alkali in the presence of different metal strips

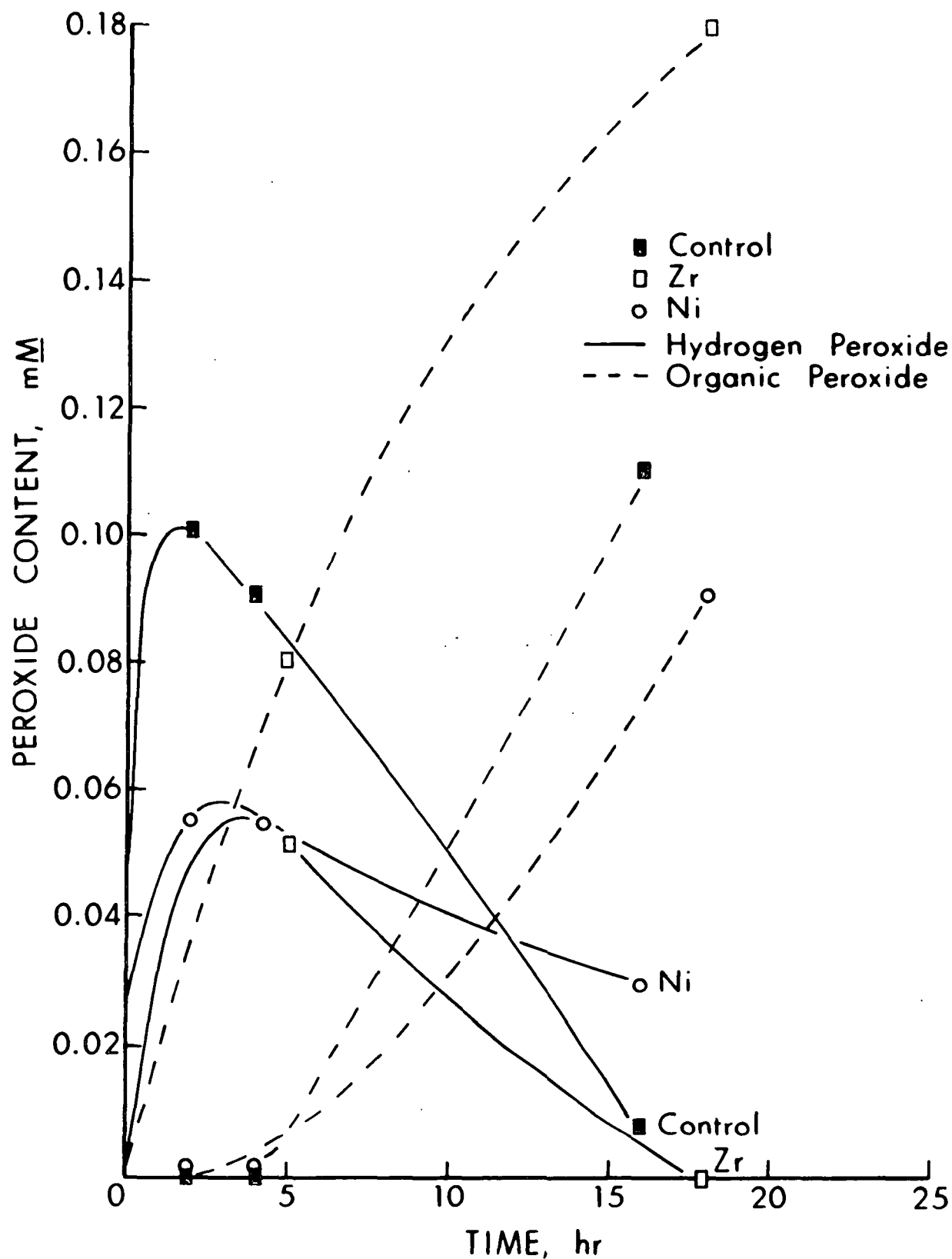


Fig. 4. The production of peroxides from the reaction of methyl β -D-glucopyranoside with oxygen and alkali in the presence of different metals